POTASSIUM

1. Introduction

Potassium [7440-09-7], K, is the third element in the alkali metal series. The name designation for the element is derived from potash, a potassium mineral; the symbol from the German name *kalium*, which comes from the Arabic *qili*, a plant. The ashes of these plants (*al qili*) were the historical source of potash for preparing fertilizers (qv) or gun powder. Potassium ions, essential to plants and animals, play a key role in carbohydrate metabolism in plants. In animals, potassium ions promote glycolysis, lipolysis, tissue respiration, and the synthesis of proteins (qv) and acetylcholine. Potassium ions are also believed to function in regulating blood pressure.

Potassium and sodium share the position of the seventh most abundant element on earth. Common minerals such as alums, feldspars, and micas are rich in potassium. Potassium metal, a powerful reducing agent, does not exist in nature.

2. Physical Properties

Potassium, a soft, low density, silver-colored metal, has high thermal and electrical conductivities, and very low ionization energy. One useful physical property of potassium is that it forms liquid alloys with other alkali metals such as Na, Rb, and Cs. These alloys have very low vapor pressures and melting points.

Potassium has three naturally occurring isotopes: ^{39}K (93.08%), ^{40}K (0.01%), and ^{41}K (6.91%). The radioactive decay of ^{40}K to argon (^{40}Ar), half-life of 10^9 years, makes it a useful tool for geological dating. Some physical properties of potassium are summarized in Table 1 (1–3).

3. Chemical Properties

Potassium has an electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$. All the alkali metals (Li, Na, K, Rb, Cs) are good reducing agents, because of the strong tendency to attain inert gas electron configuration. Reducing power increases from lithium to cesium. Cesium and rubidium are too reactive for safe handling and are not commercially available in large quantities. Potassium is the most electropositive reducing agent used in industry.

The alkali metals share many common features, yet differences in size, atomic number, ionization potential, and solvation energy leads to each element maintaining individual chemical characteristics. Among K, Na, and Li compounds, potassium compounds are more ionic and more nucleophilic. Potassium ions form loose or solvent-separated ion pairs with counteranions in polar solvents. Large potassium cations tend to stabilize delocalized (soft) anions in transition states. In contrast, lithium compounds are more covalent, more soluble in nonpolar solvents, usually existing as aggregates (tetramers and hexamers) in the form of tight ion pairs. Small lithium cations stabilize localized (hard) counteranions (see LITHIUM AND LITHIUM COMPOUNDS). Sodium chemistry is intermediate between that of potassium and lithium (see SODIUM AND SODIUM ALLOYS).

The superb reducing power of potassium metal is clearly demonstrated by its facile displacement of protons in the weakly acidic hydrocarbons (qv), amines, and alcohols (Table 2). Reactions with inorganics and gaseous elements are summarized in Table 3.

4. Preparation and Manufacture

On the laboratory scale, potassium can be prepared by the following reactions, however, these reactions are not easily adaptable to a commercial scale.

$$K_2CO_3 + 2\,C \xrightarrow{\text{heat}} 3\,CO + 2\,K^0 \tag{1}$$

$$2\,KCl + CaC_2 \xrightarrow{\text{heat}} CaCl_2 + 2\,C + K^0 \tag{2}$$

$$2\,KN_3 \xrightarrow{\text{heat}} 3\,N_2\uparrow + 2\,K^0 \tag{3}$$

In industry, chemical reduction is preferred over electrolytic processes fo rpotassium production. Application of the Down's electrolytic sodium process to produce potassium has not been successful. Potassium–sodium alloy is easily prepared by the reaction of sodium with molten KCl, KOH, or solid K_2CO_3 powder (see SODIUM AND SODIUM ALLOYS).

Mine Safety Appliances Company, USA (MSA) developed a reduction process using sodium and KCl to produce potassium metal in the 1950s (4):

$$KCl + Na^0 \leftrightarrows K^0 + NaCl \tag{4}$$

The technology is based on the rapid equilibrium established between the reactants and products at high temperatures. The equilibrium shifts to the product side when potassium is removed continuously by distillation through a packed column. This process can produce high purity potassium metal. Appropriate adjustments of conditions give a wide range of potassium–sodium alloys of specified compositions.

The commercial production equipment consists of a furnace, heat-exchanger tubes, a fractionating column packed with Rachig rings, a KCl feed, a waste removal system, and a vapor condensing system (Fig. 1).

During operation, KCl is melted and introduced through a trap to the column. Molten sodium is fed to the bottom of the column. The lower portion of the column serves as a reactor, the upper portion as a fractionator. Potassium vapor is fractionated and condensed in an air-cooled condenser with the reflux pumped back to the top of the column. Waste sodium chloride is continuously removed from the bottom of the column through a trap.

5. Shipping

Potassium of 98–99.5% purity is supplied in carbon steel or stainless steel drums and cylinders. Potassium metal is not to be stored under oil or hydrocarbons (5). Potassium–sodium alloy is shipped in carbon or stainless steel containers (3, 10, 25, 200, 750 lbs (1.36, 4.54, 11.3, 90.7, and 340-kg)) having dip tubes and valves.

Transport regulations are as follows (6):

Metal/alloy	Identification number
potassium	UN 2257
potassium–sodium alloys	UN 1422

Potassium and the alloys are classified as Hazard Class 4.3, "substances which in contact with water may emit flammable gases, solids," by U.S. Department of Transportation (DOT) regulations. A blue background label with a "Flame" pictogram, the words "Dangerous When Wet" and the number "4" is required. Quantities less than 500 g may be shipped via United Parcel Service (UPS) packaging in exemption specified in the October 1992 UPS "Guide for Shipping Hazardous Materials." Larger quantities are shipped in DOT Specification 4BW240 cylinders via common carrier, regulated under 49 CFR. Air shipments are restricted to cargo aircraft only, 15 kg (max), and packaged under packing instruction 412 of the International Air Transport Association (IATA) "Dangerous Goods Regulations" (1994) or the International Civil Aviation Organization (ICAO) "Technical Instructions for the Safe Transport of Dangerous Goods by Air" (1993–1994).

6. Economic Aspects

Total U.S. production of potassium metal is less than 1000 t/yr (7). There are few commercial producers worldwide, although some companies produce potassium captively. The more prominent producers are Callery Chemical Company Evans, City, Penn. (a division of BASF AG) and the People's Republic of China. Potassium may be manufactured in Russia as well. Strem Chemicals (U.S.) supplies small quantities in ampuls.

Potassium up to 99.99% purity can be produced by zone refining (qv) or further distillation (qv) of commercial potassium. Technical-grade potassium is minimum 99% and is packaged under nitrogen.

Smaller quantities of potassium and NaK are available in glass or metal ampuls (<100 g), or in stainless cylinders containing 12–13 kg. Potassium is also available in 84- or 209-L drums (containing 75 and 135 kg, respectively). NaK is available in cylinders containing 91 or 340 kg.

7. Analytical Methods

The principal impurity in potassium metal is sodium. Potassium's purity can be accurately determined by a melting point test (Fig. 2) or atomic absorption if necessary after quenching with alcohol and water. Traces of nonmetallic impurities such as oxygen, carbon, and hydrogen can be determined by various chemical and physical methods (1,8).

8. Health and Safety Factors

Reactions of potassium with water and oxygen are hazardous and safe handling is a concern. Potassium oxidizes slowly in air at room temperature, and it usually ignites if it sprays hot into the air. The peroxide and superoxide products may explode in contact with free potassium metal or organic materials including hydrocarbons. Thus, packaging (qv) under oils is less desirable than packaging under an inert cover gas or in a vacuum. Potassium can react with entrapped air in oils to form the superoxide. The encrustation of potassium with superoxide (as a yellow crust) developed during storage has been known to detonate by friction from cutting. Potassium encrusted with a peroxide and superoxide layer should be destroyed immediately by careful, controlled disposal (9).

Potassium forms corrosive potassium hydroxide and liberates explosive hydrogen gas upon reaction with water and moisture. Airborne potassium dusts or potassium combustion products attack mucous membranes and skin causing burns and skin cauterization. Inhalation and skin contact must be avoided. Safety goggles, full face shields, respirators, leather gloves, fire-resistant clothing, and a leather apron are considered minimum safety equipment.

Steam (qv) may be used to destroy potassium residues. It is imperative that equipment be designed to permit substantially complete drainage of potassium metal prior to steam cleaning. Precautions must also be taken to avoid hydrogen–air explosions. Small quantities of the metal can be safely destroyed under nitrogen by adding *t*-butyl alcohol or high boiling alcohols, followed by methanol, and then water. The caustic aqueous potassium waste should be disposed of in compliance with local regulations.

8.1. Fire Fighting. Potassium metal reacts violently with water releasing flammable, explosive hydrogen gas. Burning potassium is difficult to extinguish. Dry soda ash, dry sodium chloride, or Ansul's Met-L-X must be used for potassium or potassium alloy fires. Water, foam, carbon dioxide, or dry chemical fire extinguishers should never be employed. A NIOSH/MSHA approved self-contained breathing apparatus with full facepiece operated in a positive pressure mode and full protective clothing should be worn when removing spills and fighting fire (8,10).

9. Uses

Historically, potassium metal was used by the Mine Safety Appliances Company (former parent company of Callery Chemical Company) to develop potassium superoxide [12030-88-5], KO_2, for use as an oxygen source in self-contained breathing equipment (see OXYGEN-GENERATION SYSTEMS). Greater understanding of potassium chemistry since the 1950s and 1960s has led to numerous additional and important industrial applications (11–18). Potassium, potassium–sodium alloys, and potassium derivatives such as alkoxides, amides, and the hydride are extensively used, both industrially and academically, to synthesize organic and inorganic materials.

9.1. Potassium–Sodium Alloys.

Potassium–sodium alloys, NaK, represent a use for potassium metal. Physical properties such as a wide range of compositions in liquid–metal forms (see Fig. 2), combined with excellent thermal and electrical conductivities, render these alloys ideal for use as heat-exchange fluids (19,20), cooling liquids in hollow valve stems (21), contact liquids for high temperature thermostats and homopolar generators, and hydraulic fluids (qv) (22). Potassium and potassium–sodium alloys were also used as working fluids on power plant topping cycles during the 1940s and 1950s.

A eutectic at 77.2% potassium has a freezing point of $-12.56^\circ C$ (see Fig. 2). A ternary eutectic (3% Na–24% K–73% Cs) melts at $-76^\circ C$. The physical properties of NaK for 78 wt% K, 22 wt% Na are summarized in Table 4.

Chemically the liquid NaK alloy, usually used as a dispersion and on an inert support, provides more reactive surface area than either potassium or sodium metal alone, thus enhancing the reducing reactivity and permitting reactions to proceed at lower (eg, $-12^\circ C$) temperatures. NaK alloys are suitable for chemical reactions involving unstable intermediates such as carbanions and free radicals.

NaK alloys have been used successfully in the following applications: side-chain alkylation of toluenes (see TOLUENE) and xylenes (see XYLENES AND ETHYLBENZENE) (23); isomerization of α-olefins to internal olefins (see OLEFINS, HIGHER) (24,25); free-radical (26) and condensation (27–30) polymerization; reduction of metal halides to active metal powder (31); reduction of organic functional groups such as arenes, ketones (qv), aldehydes (qv), and alkyl halides (32,33); cleavage of functional groups containing C–X, C–O, and O–S bonds (34–38); interesterification of tallow with cottonseed oil to improve pour and clarification temperatures (39,40) (see COTTON); and impurity scavenging of acetylenic and allenic contaminants (41).

9.2. Potassium Bases.

Potassium metal is used to prepare potassium bases from reactions of the metal with alcohols and amines.

Potassium Alkoxides.

The most widely used potassium bases are potassium *tert*-butoxide [865-47-4] (KTB) and potassium *tert*-amylate [41233-93-6] (KTA). These strong alkoxide bases offer such advantages as base strength ($pK_a = 18$), solubility (Table 5), regio/stereoselectivity because of bulky *tert*-alkyl groups, and stability because of the lack of α-protons. On storage, KTB and KTA have long shelf lives under inert atmosphere (see ALKOXIDES, METAL).

KTB and KTA are superior to alkali metal hydrides for deprotonation reactions because of the good solubilities, and because no hydrogen is produced or oil residue left upon reaction. Furthermore, reactions of KTA and KTB can be performed in hydrocarbon solvents as sometimes required for mild and nonpolar reaction conditions. Potassium alkoxides are used in large quantities for addition, esterification, transesterification, isomerization, and alkoxylation reactions.

Potassium Amides. The strong, extremely soluble, stable, and nonnucleophilic potassium amide base (42), potassium hexamethyldisilazane [40949-94-8] (KHMDS), $KN[Si(CH_3)]_2$, $pK_a = 28$, has been developed and commercialized. KHMDS, ideal for regio/stereospecific deprotonation and enolization reactions for less acidic compounds, is available in both THF and toluene solutions. It has demonstrated benefits for reactions involving kinetic enolates (43), alkylation and acylation (44), Wittig reaction (45), epoxidation (46), Ireland-Claison rearrangement (47,48), isomerization (49,50), Darzen reaction (51), Dieckmann condensation (52), cyclization (53), chain and ring expansion (54,55), and elimination (56).

Potassium 3-aminopropylamide [56038-00-7] (KAPA), $KNHCH_2CH_2CH_2{-}NH_2$, $pK_a = 35$, can be prepared by the reaction of 1,3-diaminopropane and potassium metal or potassium hydride [7693-26-7] (57–59). KAPA powder has been known to explode during storage under nitrogen in a drybox, and is therefore made *in situ*. KAPA is extremely effective in converting an internal acetylene or allene group to a terminal acetylene (60) (see ACETYLENE-DERIVED CHEMICALS).

9.3. Potassium Graphite. Potassium, rubidium, and cesium react with graphite and activated charcoal to form intercalation compounds: C_8M, $C_{24}M$, $C_{36}M$, $C_{48}M$, and $C_{60}M$ (61,62). Potassium graphite [12081-88-8], C_8K, made up of gold-colored flakes, is prepared by mixing molten potassium with graphite at 120–150°C.

Potassium graphite is a powerful solid reducing agent because of the free electrons from the ionized potassium trapped inside the graphite lattice. In packed beds, it can effectively eliminate undesired organic contaminants such as halogenated hydrocarbon impurities from gas streams and liquid solutions. The scope of its reducing reactions includes (61) Birch-type reactions of α,β-unsaturated ketones, carboxylic acids, and Schiff's bases; reductive cleavage of vinylic and allylic sulfones; selective alkylation of aliphatic esters, imines, and nitriles; and reductive decyanation of nitriles. Potassium graphite has been used to prepare active metals supported on graphite (62,63): Zn–Gr [69704-06-9] for Reformatsky reactions, Sn–Gr [89248-61-3] for allylic organometallics, Ti–Gr [6970-05-8] for coupling carbonyl compounds, Fe–Gr [55957-21-6] for debromination, Pd–Gr [59873-73-3] for vinylic and allylic substitution, and Pd–Gr, Ni–Gr [59873-69-7] for hydrogenation, etc. Potassium graphite has also been applied in polymerization reactions (see CARBON, SURVEY).

9.4. Potassium Hydride. Potassium hydride [7693-26-7], KH, made from reaction of molten potassium metal with hydrogen at ca 200°C, is supplied in an oil dispersion. KH is much more effective than NaH or LiH for enolization reactions (64,65). Use of KH as a base and nucleophile has been reviewed (66).

A noteworthy development is the use of KH for complexing alkylboranes and alkoxyboranes to form various boron hydrides used as reducing agents in the pharmaceutical industry. Potassium tri-*sec*-butylborohydride [54575-50-7], $KB(CH(CH_3)C_2H_5)_3H$, and potassium trisiamylborohydride [67966-25-0], $KB(CH(CH_3)CH(CH_3)_2)_3H$, are useful for the stereoselective reduction of ketones (67) and for the conjugate reduction and alkylation of α,β-unsaturated ketones (68).

9.5. Potassium Superoxide. Potassium, rubidium, and cesium form superoxides, MO_2, upon oxidation by oxygen or air. Sodium yields the peroxide,

Na_2O_2; lithium yields the oxide, Li_2O, when oxidized under comparable conditions. Potassium superoxide [12030-88-5], KO_2, liberates oxygen in contact with moisture and carbon dioxide (qv). This important property enables KO_2 to serve as an oxygen source in self-contained breathing equipment.

The unique chemical behavior of KO_2 is a result of its dual character as a radical anion and a strong oxidizing agent (69). The reactivity and solubility of KO_2 is greatly enhanced by a crown ether (70). Its usefulness in furnishing oxygen anions is demonstrated by its applications in SN_2-type reactions to displace methanesulfonate and bromine groups (71,72), the oxidation of benzylic methylene compounds to ketones (73), and the syntheses of α-hydroxyketones from ketones (74).

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KUEN-WAI CHIU
Callery Chemical Company

Updated by Staff

Table 1. **Physical Properties of Potassium**

Property	Value
atomic weight	39.102
atomic radius, pm	235
ionic radius, pm	133
Pauling electronegativity	0.8
crystal lattice	body-centered cubic
analytical spectral line, nm	766.4
melting point, °C	63.7
boiling point, °C	760
density, at 20°C, g/cm^3	0.86
specific heat, J/(g·K)[a]	0.741
heat of fusion, J/g[a]	59.591
heat of vaporization, kJ/g[a]	2.075
electrical conductance, at 20°C, μS	0.23
surface tension, at 100°C, mN/m(=dyn/cm)	86
thermal conductivity, at 200°C, W/(m·K)	44.77

[a] To convert J to cal, divide by 4.184.

Table 2. **Potassium Products from Hydrocarbons, Amines, and Alcohols**

Starting material	pK_a[a]	Product
1,3-diaminopropane	35	$KNH(CH_2)_3NH_2$
ammonia	35	KNH_2
hexamethyldisilazane	28	$KN[Si(CH_3)_3]_2$
aniline	27	$KNHC_6H_5$
acetylene	25	$KC\equiv CH$
tert-butyl alcohol	18	$KOC(CH_3)_3$
methanol	16	$KOCH_3$
phenol	10	KOC_6H_5

[a] Values correspond to the pK_a of the conjugate acid of the potassium base.

Table 3. **Chemical Reactions of Potassium**

Reactant	Reaction	Product
H_2	begins slowly at ca 200°C; rapid above 300°C	KH
O_2	begins slowly with solid; fairly rapid with liquid	K_2O, K_2O_2, KO_2
H_2O	extremely vigorous and frequently results in hydrogen–air explosions	KOH, H_2
$C_{(graphite)}$	150–400°C	KC_4, KC_8, KC_{24}
CO	forms unstable carbonyls	(KCO)
NH_3	dissolves as K; iron, nickel, and other metals catalyze in gas and liquid phase	KNH_2
S	molten state in liquid ammonia	K_2S, K_2S_2, K_2S_4
F_2, Cl_2, Br_2	violent to explosive	KF, KCl, KBr
I_2	ignition	KI
CO_2	occurs readily, but is sometimes explosive	CO, C, K_2CO_3

Table 4. **Physical Properties of NaK**[a]

Parameter	Value
melting point, °C	−12.6
boiling point[b], °C	785
electrical resistance, μΩ·cm	
at −12.6°C	33.5
20°C	38.0
density at 20°C, g/cm³	0.867
thermal conductivity, W/(m·K)	
at 20°C	2.18×10^{-3}
550°C	2.62×10^{-3}
specific heat, J/(g·K)[c]	
at −12.6°C	0.975
100°C	0.937

[a] 78 wt% K, 22 wt% Na.
[b] Value is estimated.
[c] To convert J to cal, divide by 4.184.

Table 5. **Solubilities of KTA and KTB at 25°C, wt%**

Solvent	KTA	KTB
tetrahydrofuran	>50	44
2-methoxyethyl ether	47	42
tert-butyl methyl ether	~30	2.0
toluene	36	2.3
cyclohexane	27	0.4
hexane	30	0.3

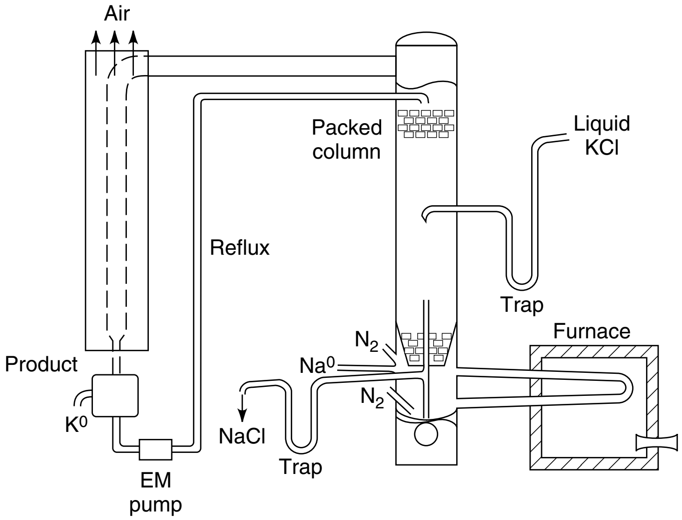

Fig. 1. Schematic diagram for the commercial production of potassium from sodium and potassium chloride. EM = electromagnetic.

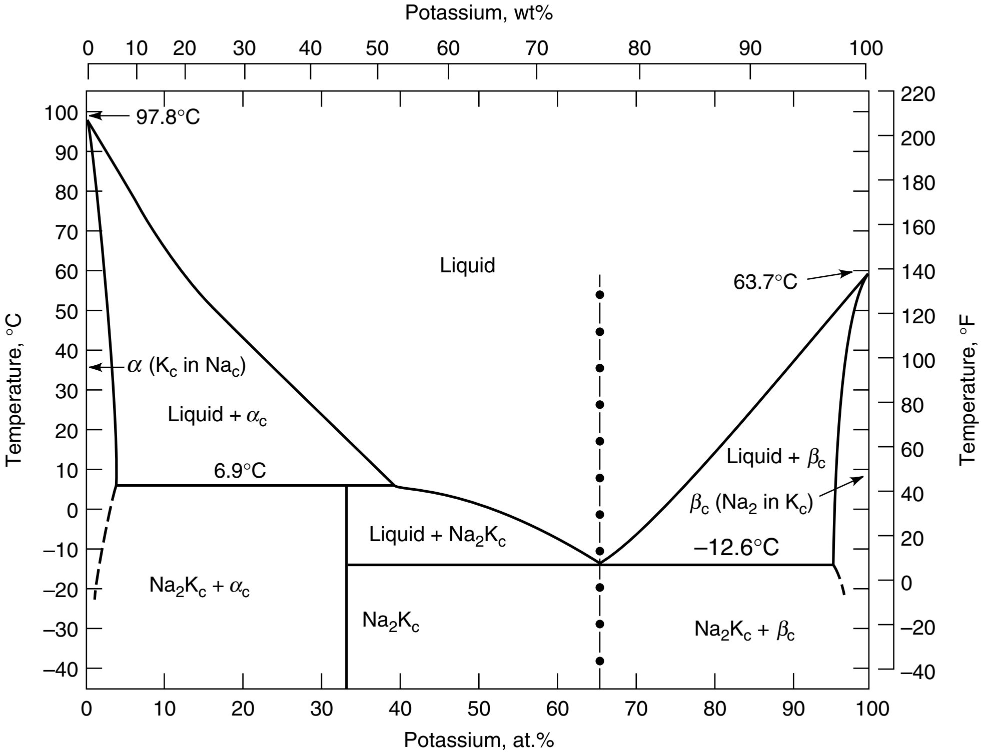

Fig. 2. Sodium–potassium equilibrium diagram where (-•-) represents the eutectic condition: 67.3 at.%, 77.8 wt% (6). α and β represent distinct solid phases; c = crystalline.